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This paper was prepared for submittal to the
12th International Symposium on Plasma Chemistry
Minneapolis, MN
August 21-25, 1995

May 1995



Lawrence
Livermore
National
Laboratory

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OH GENERATION IN STEAM-AIR PULSED CORONA

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The measurement of OH concentration in a pulsed corona discharge through a steam-air mixture is compared with a chemical kinetics model. The original motivation was to develop a technological hydroxylizer for oxidizing gas pollutants to acids. Time dependent measurements of the 3064 Å emission of OH indicate a production of nearly 4 ppm ($\approx 10^{14} \text{ cm}^{-3}$) within a spark. This measurement was accomplished by a 1 ns resolution photomultiplier with a 100 Å filter centered at 3080 Å. The discharge occurs across a 1 cm coaxial gap between a central anode tube and an outer cylindrical cathode cased in glass and at ground potential. The water-air mixture is of equal proportions and at 1 atmosphere. Pulsed voltage of 38 kV and 60 ns risetime produces a 60 A, 20 ns spark. The model predicts comparable OH production by dissociation in the air-water mixture after 100 ns of $10^{12} \text{ electrons/cm}^3$. The electron density is set to zero during the subsequent 100 μs in the model, and thereafter OH is seen as a short-lived reaction product of HO_2 with O and N atoms. The sequence of reaction is: 100 ns of dissociation to peak OH concentration, 0.2 μs for hydrogen atom loss and HO_2 formation, 20 μs for O atom loss and O_3 formation, beyond 20 μs NO formation from N atoms with OH and HO_2 . In the model HO_2 ultimately decays by slowly forming H_2O_2 , so it may be viewed as a stable fuel which produces OH when combined with atomic oxygen or nitrogen.

Introduction and Experiment

This work compares the measurement of OH concentration in a pulsed corona discharge through a steam-air mixture, and a chemical kinetics model. The original motivation was to utilize OH for gas processing applications, [1].

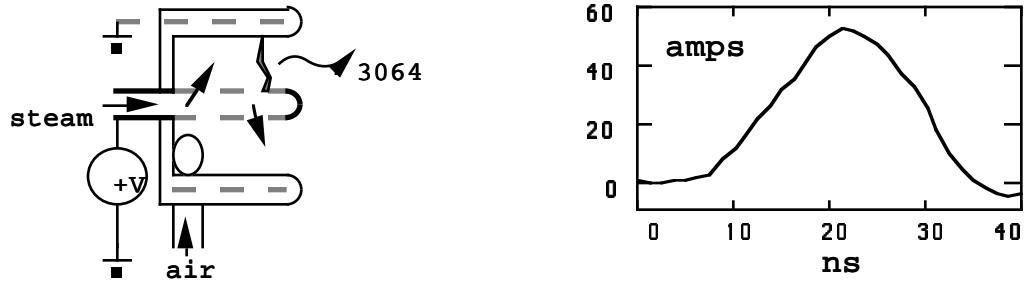


Figure 1: Schematic of coaxial-barrier steam-air discharge, and a sample current pulse

The discharge occurs across a 1 cm coaxial gap between a central anode tube (0.64 cm in diameter, 5 cm long), and an outer cylindrical cathode mesh (2.5 cm diameter) cased in glass and at ground potential. Steam is introduced through twenty-four 0.2 mm holes along the anode. Air is introduced at the base of the discharge as a swirl flow of 20 liters/minute. The water-air mixture is of equal proportions and at 1 atmosphere. Pulsed voltage of 38 kV and 60 ns risetime produces a 60 A, 20 ns spark.

Figure 2 shows a measurement of the 3064 Å emission of OH during the current pulse.

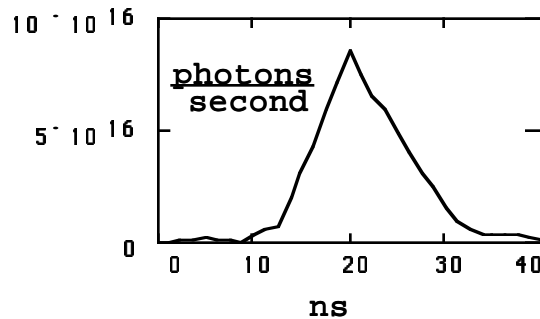


Figure 2: Measurement of OH 3064 Å emission.

This pulse represents a total of 10^9 photons. As corona streamer diameters are between 20 to 100 microns, [2], the streamer volume in this experiment is below 10^{-4} cm^3 which indicates an OH concentration of up to 10^{14} cm^{-3} . By taking 1 ppm as equal to one millionth the density of dry air, or $2.69 \times 10^{13} \text{ cm}^{-3}$ for

comparative purposes, the OH concentration in the experiment is between 3 and 4 ppm. The measurement was accomplished by a photomultiplier with a temporal resolution of 1 ns, and a 100 Å bandpass filter centered at 3080 Å.

Chemical Kinetics Model

The chemical kinetics model includes thirty four reactions involving the twelve species: H₂, O₂, NO, N₂, H₂O, H, O, N, OH, HO₂, H₂O₂, and O₃. Rate coefficients for dissociation are calculated from a Boltzmann model [3], all other reaction rates are taken from Mätzing [4] at a temperature of 300 K. In this model all species are assumed to be in the gas phase, no attempt is made to model the actual mixture of air, water vapor, fog, and mist. Electrons dissociate hydrogen, oxygen, nitrogen, water, and NO. Ozone only appears as a sink, there are no oxidation reactions by ozone. The initial mixture is comprised of equal concentrations of water and air each at $2.69 \times 10^{19} \text{ cm}^{-3}$, where the model air is composed of 79% nitrogen and 21% oxygen. During the initial interval of 100 ns electron density is held constant at 10^{12} cm^{-3} , and the dissociation rate coefficients are specified for a Townsend parameter of 125 Td. The electron density is then set to zero and the system allowed to evolve for 100 μs. Solution is effected by simultaneous forward integration of twelve rate equations, 2000 time steps are used in each of the two time domains ($\Delta t = 0.05 \text{ ns}$ for 100 ns, then $\Delta t = 50 \text{ ns}$ for 100 μs). Results are shown in ppm as defined earlier.

The chemical kinetics model predicts the same OH production from the air-water mixture after 100 ns of $10^{12} \text{ electrons/cm}^3$. In the subsequent 100 μs of electron-free evolution, OH is seen as a short-lived product of reactions between HO₂ with oxygen and nitrogen atoms, until these atoms have recombined into molecules, and the HO₂ has been converted to H₂O₂. Note reference [5].

During the initial 100 ns discharge interval 32 ppm of O atoms are generated, or eight times more than the production of OH. Figure 4 summarizes the other significant species.

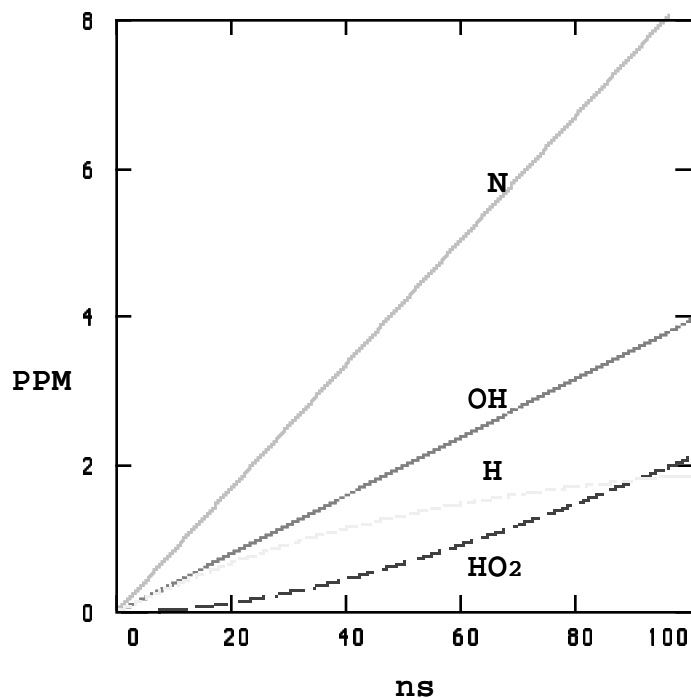


Figure 4: Model discharge interval (also 32 ppm O)

The subsequent 100 μs of electron-free evolution has three distinct phases extending to: 0.2 μs , 20 μs , and beyond 20 μs . During the first 0.2 μs hydrogen atoms disappear by combining with O_2 to form HO_2 , see Figure 5 (note log scale).

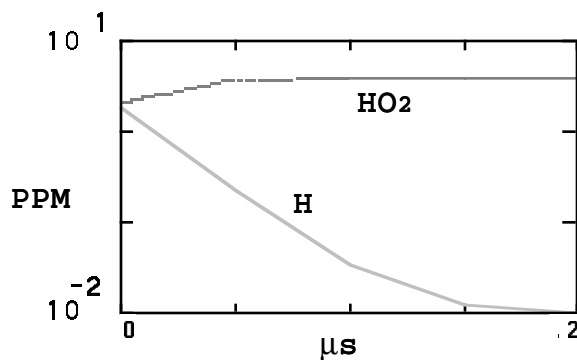


Figure 5: Hydrogen atom loss

During the subsequent evolution a cycle is observed in which OH reacts with atoms to form H and molecules, the hydrogen atoms are quickly converted to HO_2 , and HO_2 reacts with atoms to produce OH and molecules.

Oxygen atoms dominate this cycle for 20 μs until ozone formation has scavenged them, then only the slowly recombining nitrogen atoms are involved. Oxygen atoms favor a higher concentration of OH versus HO_2 by their aggressive oxidation of HO_2 , while nitrogen atoms favor HO_2 over OH.

By 100 μs over 2 ppm of NO has formed, which is nearly 10% of the ozone concentration. A similar effect was observed during experiments. Figures 6 and 7 summarize these results.

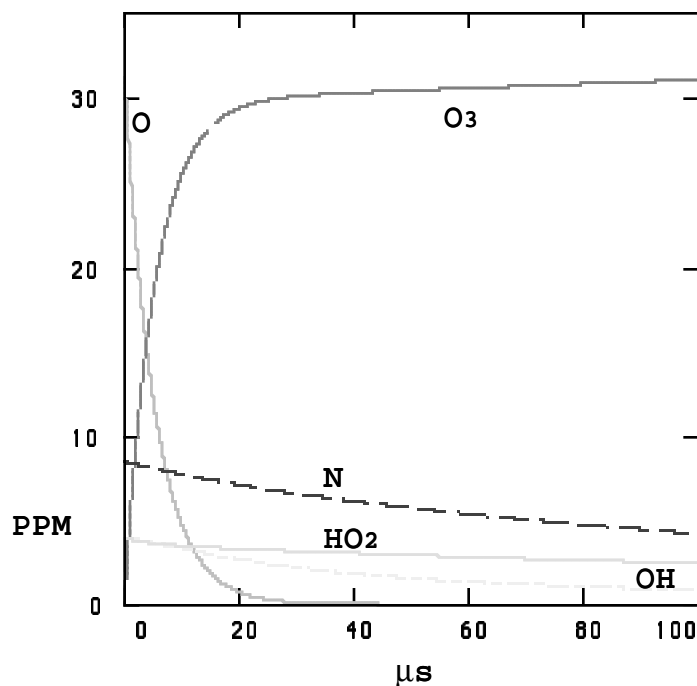


Figure 6: Post-discharge evolution

In the model HO_2 decays by the slow process of H_2O_2 formation, so it may be viewed as a stable fuel which produces the transitory species OH when combined with atomic oxygen or nitrogen.

This work was performed under the auspices of the U.S. Dept. of Energy at LLNL under contract no. W-7405-Eng-48.

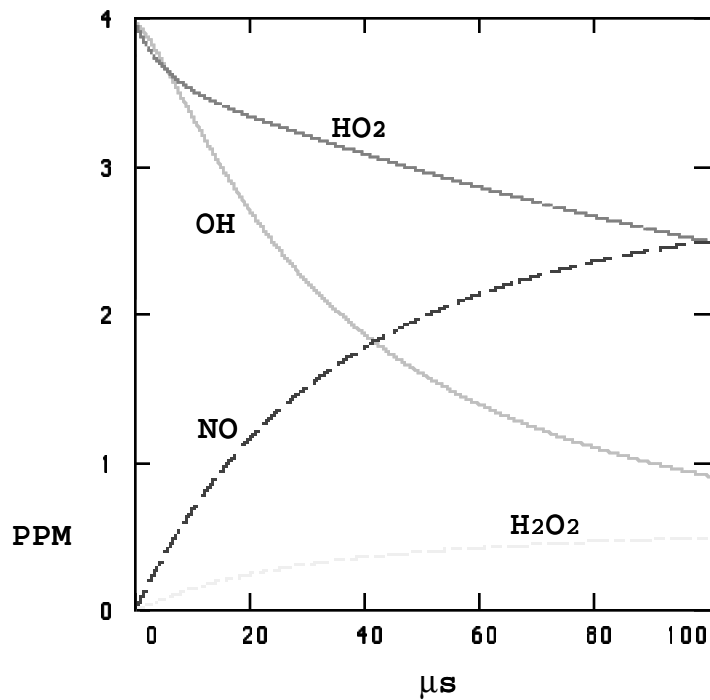


Figure 7: Post-discharge evolution of OH.

References

- [1] B. Chang, M. Garcia, this symposium.
- [2] J. Chang, P. Lawless, T. Yamamoto, "Corona Discharge Processes," *IEEE Trans. Plasma Sci.*, vol. 19, pp. 1152-1166, Dec. 1991.
- [3] M. Garcia, B. Chang, "Analytical Boltzmann Moments for Electrons in N₂-O₂-H₂O Gas Mixtures," *IEEE Int. Conf. on Plasma Sci. (Santa Fe, NM)*, June 1994.
- [4] H. Mätzing, "Chemical Kinetics of Flue Gas Cleaning by Irradiation with Electrons," *Advances in Chemical Physics Volume LXXX*, I. Prigogine, S. Rice, Eds., John Wiley & Sons, New York, 1991, pp. 315-402.
- [5] F. Kaufman, F. Del Greco, "Fast Reactions of OH Radicals," *Ninth (International) Symposium on Combustion, at Cornell University 1962*, Academic Press, New York, 1963, pp. 659-668.

